

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-201327

(43)Date of publication of application : 04.08.1995

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(51)Int.Cl.

H01M 4/32

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(21)Application number : 05-352525

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(22)Date of filing : 29.12.1993

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(54) NON-SINTERED NICKEL POSITIVE ELECTRODE FOR ALKALINE STORAGE BATTERY

(57)Abstract:

PURPOSE: To heighten the filling density and use efficiency of an active material.

CONSTITUTION: Regarding a non-sintered nickel positive electrode prepared by filling the pores of a current collector having a three-dimensional porous structure with an active material for alkaline storage batteries; 100 parts by weight of nickel hydroxide particles with 7-12 $\mu$ m average particle size and bearing a conductive layer consisting of 0.5-2 parts by weight of calcium hydroxide and 5-15 parts by weight of cobalt hydroxide are used as the active material. Consequently, the capacity of an alkaline storage battery is increased by using the resulting nickel positive electrode for the battery.

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## LEGAL STATUS

[Date of request for examination] 22.12.1999

[Date of sending the examiner's decision of rejection] 15.01.2002

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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**CLAIMS**

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[Claim(s)]

[Claim 1] The non-sintering nickel positive electrode for alkaline batteries characterized by forming the conductive layer to which said active material becomes the particle front face of the nickel hydroxide 100 weight section with a mean particle diameter of 7-12 micrometers from a calcium hydroxide 0.5 - 2 weight sections, and cobalt hydroxide 5 - 15 weight sections in the non-sintering nickel positive electrode for alkaline batteries which comes to fill up an active material in the hole of the charge collector which has a three-dimension vesicular structure.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to amelioration of said active material aiming at obtaining the detailed non-sintering nickel positive electrode for alkaline batteries with high pack density and utilization factor of an active material with respect to the non-sintering nickel positive electrode for alkaline batteries.

[0002]

[Description of the Prior Art] The non-sintering nickel positive electrode which uses nickel hydroxide as an active material is put in practical use as a positive electrode of alkaline batteries, such as a nickel cadmium battery. It is made to react, throwing in nickel nitrate in an alkali water solution, and carrying out stirring mixing as the manufacture approach of the above-mentioned nickel hydroxide, and the method of obtaining spherical nickel hydroxide as settlings is proposed. However, as it is, since the conductivity of nickel hydroxide was not good for the positive electrode using the nickel hydroxide obtained by this approach as an active material, the utilization factor of a positive electrode was low to it, and so, there was a problem that capacity was small in it.

[0003] A calcium nitrate is thrown in with a nickel nitrate water solution in an alkali water solution in order to solve this problem, coprecipitation of nickel hydroxide and the calcium hydroxide is carried out, and the method of making a calcium hydroxide contain is proposed in order to raise conductivity in the powder of nickel hydroxide (coprecipitation method).

[0004] However, there was a problem that the calcium-hydroxide content nickel hydroxide produced with this coprecipitation method had the low pack density of an active material to the non-sintering nickel positive electrode using this as an active material compared with the nickel hydroxide (usually particle size of about 6 micrometers or more) produced by the approach of settling independently the nickel hydroxide mentioned above since particle size was as small as 2-3 micrometers and bulk density was also small.

[0005] Moreover, since a calcium hydroxide distributes and existed not only in the front face of an active material (calcium-hydroxide content nickel hydroxide) but in the interior when it produces with a coprecipitation method, conductivity had the problem that did not improve so much and the utilization factor of an active material so did not improve so much, either. Although the attempt with which it is filled up in the hole of the charge collector which carries out addition mixing of the electric conduction agents, such as cobalt hydroxide, separately into the slurry containing an active material (calcium-hydroxide content nickel hydroxide), and has the shape of sponge and a fibrous three-dimension vesicular structure about this problem is proposed, since it is most difficult to make homogeneity distribute cobalt hydroxide and calcium-hydroxide content nickel hydroxide in the hole of a charge collector, the actual condition has come to obtain a nickel positive electrode with the utilization factor of an active material high enough.

[0006] This invention is made in view of the above situation, and the place made into the purpose is

to offer the non-sintering nickel positive electrode for alkaline batteries with high pack density and utilization factor of an active material.

[0007]

[Means for Solving the Problem] In the non-sintering nickel positive electrode for alkaline batteries with which the non-sintering nickel positive electrode for alkaline batteries concerning this invention for attaining the above-mentioned purpose (the "this invention electrode" is called hereafter.) comes to fill up an active material in the hole of the charge collector which has a three-dimension vesicular structure, the conductive layer to which said active material becomes the particle front face of the nickel hydroxide 100 weight section with a mean particle diameter of 7-12 micrometers from a calcium hydroxide 0.5 - 2 weight sections, and cobalt hydroxide 5 - 15 weight sections is formed.

[0008] The mean particle diameter of nickel hydroxide is regulated by 7-12 micrometers. While the particle size of an active material is too small in the case of less than 7 micrometers and being hard coming to fill this up in the hole of a charge collector Since bulk density becomes small, on the other hand, it is 12 micrometers (since the thickness of a conductive layer is usually about 1 micrometer, the mean particle diameter of the active material particle in this case is usually set to about 13 micrometers.). Since particle size is too large although the bulk density of nickel hydroxide becomes large when it exceeds, and it is hard coming to be filled up in the hole of a charge collector, in any case, the pack density of an active material is because it becomes low.

[0009] Nickel hydroxide is obtained as precipitate by throwing in nickel nitrate, a nickel sulfate, etc. in an alkali water solution, and carrying out stirring mixing. In order to obtain nickel hydroxide with a mean particle diameter of 7-12 micrometers, it is necessary to adjust suitably pH of an alkali water solution, agitating speed, mixing time, etc. For example, what is necessary is just to be pH [ of an alkali water solution ]  $11 \pm 0.1$ , agitating speed 800rpm, and mixing time 60 hours, in producing  $11 \pm 0.1$  and agitating speed for pH of an alkali water solution and producing 12 hours, then the nickel hydroxide powder whose mean particle diameter it is good and is 12 micrometers for 400rpm and mixing time, when mean particle diameter produces the nickel hydroxide powder which is 7 micrometers.

[0010] Since the case of under the 0.5 weight sections does not yet have enough conductivity, the rate of the calcium hydroxide in a conductive layer is regulated by 0.5 - 2 weight section to the nickel hydroxide 100 weight section because the rate of the nickel hydroxide in an active material decreases and the fall of capacity is caused, when the utilization factor of an active material does not fully improve but 2 weight sections are exceeded on the other hand.

[0011] Moreover, it depends on the same reason [ that the rate of the cobalt hydroxide in a conductive layer is also regulated by 5 - 15 weight section to the nickel hydroxide 100 weight section ] as the above. That is, since the case of under 5 weight sections cannot fully raise conductivity, when improvement in the utilization factor of an active material is not fully attained but exceeds 15 weight sections on the other hand, it is because the rate of the nickel hydroxide in an active material decreases and the fall of capacity is caused.

[0012]

[Function] Since the active material of a moderate particle size is used, the pack density of an active material becomes high. Moreover, since the conductive layer containing the calcium hydroxide and cobalt hydroxide of the specified quantity exists on the surface of an active material, the conductivity of an active material improves and, as a result, the utilization factor of the active material of a nickel positive electrode becomes high.

[0013]

[Example] It is possible to change this invention suitably in the range which is not limited at all by the following example and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0014] (Example 1) Threw in the nickel nitrate water solution in the water solution adjusted to pH

11\*\*0.1 with a sodium hydroxide and ammonia, and it was made to react for 24 hours, carrying out stirring mixing by 600rpm, and spherical nickel hydroxide was obtained.

[0015] Subsequently, threw in the above-mentioned nickel hydroxide powder, the cobalt nitrate water solution, and the calcium nitrate water solution in the water solution adjusted to pH 11\*\*0.1 with a sodium hydroxide and ammonia, and it was made to react for 24 hours, carrying out stirring mixing by 600rpm, and the conductive layer which consists of cobalt hydroxide and a calcium hydroxide was formed in the particle front face of nickel hydroxide, and this was rinsed, it dried, and the active material was obtained.

[0016] When ICP analyzed the rate of the cobalt hydroxide to the nickel hydroxide 100 weight section in a conductive layer, and a calcium hydroxide, they were 10 weight sections and 1 weight section, respectively. In addition, ICP also analyzes all the ratios of each metal mentioned later.

[0017] Next, the water solution of the above-mentioned active material 100 weight section and the carboxymethyl-cellulose 0.5 weight section as a thickener (after electrode production is committed as a binder.) was kneaded, it considered as the slurry, foaming metal was filled up with this slurry, and this invention electrode NA1 was produced.

[0018] A nickel nitrate water solution, a cobalt nitrate water solution, and a calcium nitrate water solution (Example 1 of a comparison) By the mole ratio 98:1:1 of nickel:cobalt:calcium It supplies in the water solution adjusted to pH 11\*\*0.1 with a sodium hydroxide and ammonia. It is made to react for 24 hours, carrying out stirring mixing by 600rpm, and coprecipitation of nickel hydroxide, cobalt hydroxide, and the calcium hydroxide was carried out, and this coprecipitate was rinsed, it dried, and the reference electrode NB1 was produced like the above-mentioned example 1 except having obtained the active material.

[0019] [Utilization factor of an active material] After assembling the trial cel and charging this trial cel with the current of 1/10C like the after-mentioned for 16 hours using this invention electrode NA1 and a reference electrode NB1, it discharged to discharge-final-voltage 0.8V with the current of 1/3C, the discharge capacity of each trial cel was measured, and the utilization factor of the active material of the positive electrode of each trial cel was searched for based on the following formula. A result is shown in Table 1.

[0020] It piles up in the form which uses the <assembly of trial cel> this invention electrode NA1, and a reference electrode NB1 as a test electrode (positive electrode), and carries out full opposite through a nylon separator by making into a counter electrode the paste type cadmium pole which has a sufficiently big electrochemistry capacity to this test electrode. This is put into a polyethylene bag and \*\*\*\*\* (40Kgf) is applied from both sides. The specific gravity 1.23KOH water solution was put into this, and the open sand mold single electrode cel was produced.

[0021] Discharge capacity (mAh) x100of utilization factor (%) = trial cel of <formula of utilization factor of active material> active material/[the geometric capacity (mAh/g) per active material (weight g) x unit active material weight]

Geometric capacity per unit active material weight (mAh/g) = constituent 1 (weight of the constituent 3 per 1g of geometric capacity x active materials of the weight (wt%) + constituent 3 (calcium2 (OH)) of the constituent 2 per 1g of geometric capacity x active materials of the weight (wt%) + constituent 2 (Co2 (OH)) of the constituent 1 per 1g of geometric capacity x active materials of nickel (OH)2 (wt%))

[0022] For example, they are nickel(OH) 2 289.0 mAh/g, Co(OH) 2 288.3 mAh/g, and calcium(OH) 2 723.4 mAh/g.

[0023]

[Table 1]

電極	活物質の利用率 (%)
NA1	102
NB1	95

[0024] As shown in Table 1, a reference electrode NB1 has [ this invention electrode NA1 ] the utilization factor of an active material as low as 95% to a thing with the as high utilization factor of an active material as 102%.

[0025] [The mean particle diameter of an active material, the tap bulk density of an active material, and pack density of an active material] The mean particle diameter in the FISHA size of the active material used for production of each positive electrode of this invention electrode NA1 and a reference electrode NB1 and tap bulk density, and the pack density of the active material of this invention electrode NA1 and a reference electrode NB1 were investigated. A result is shown in Table 2. In addition, since the mean particle diameter and tap bulk density of nickel hydroxide itself before forming a conductive layer in the active material used for this invention electrode NA1 were also investigated, the result is also collectively shown in Table 2.

[0026]

[Table 2]

電極		平均粒径 ( $\mu\text{m}$ )	タップ嵩密度 ( $\text{g/cc}$ )	充填密度 ( $\text{g/cc}$ )
NA1	水酸化ニッケル	9.1	2.3	——
	活物質	9.5 ~ 10.1	2.4 ~ 2.6	2.80
NB1		3.2	1.3	2.10

[0027] The pack density of the active material of a reference electrode NB1 is low in cc and 2.10g /to a thing with the pack density of the active material of this invention electrode NA1 high in cc and 2.80g /. This is based on the reason shown below.

[0028] The mean particle diameter of the nickel hydroxide used for this invention electrode NA1 is 9.1 micrometers, and the mean particle diameter of an active material is 9.5–10.1 micrometers. All have large mean particle diameter. Moreover, the tap bulk density of nickel hydroxide is 2.3g/cc, and the tap bulk density of an active material is 2.4–2.6g/cc. All have large tap bulk density. On the other hand, the mean particle diameter of the active material used for the reference electrode NB1 is as small as 3.2 micrometers, and its tap bulk density is small in cc and 1.3g /. The difference of the pack density of the active material of this invention electrode NA1 and a reference electrode NB1 is based on the size of such mean particle diameter and bulk density.

[0029] the cobalt hydroxide to [nickel hydroxide -- comparatively -- \*\* -- related] with the utilization factor of an active material -- this invention electrode and the reference electrode were produced like the example 1 except having used the active material (each calcium hydroxide being 1 weight section) of the cobalt hydroxide to the nickel hydroxide 100 weight section which is 0 weight section, 5 weight sections, 15 weight sections, or 20 weight sections comparatively. Subsequently, the trial cel was assembled like the point using these this invention electrode and the reference electrode. And charge and discharge were carried out on the same conditions as the point, the utilization factor of an active material was searched for from the above-mentioned formula, and the relation of the rate of cobalt hydroxide and the utilization factor of an active material over nickel hydroxide was investigated. A result is shown in drawing 1 . In addition, the result about this invention electrode NA1 (cobalt hydroxide 10 weight section) is also shown in drawing 1 .

[0030] drawing 1 -- the utilization factor of the active material of each electrode, and the cobalt hydroxide in a conductive layer -- comparatively -- \*\* -- relation -- an axis of ordinate -- the utilization factor (%) of an active material -- moreover, it is the graph by which weight number of copies of the cobalt hydroxide in the conductive layer to the nickel hydroxide 100 weight section was taken and shown on the axis of abscissa, and as shown in this drawing, when the rate of the cobalt hydroxide in the conductive layer to the nickel hydroxide 100 weight section is made into 5 – 15 weight section, it turns out that the utilization factor of an active material can be made high.

[0031] the calcium hydroxide to [nickel hydroxide -- comparatively -- \*\* -- related] with the utilization factor of an active material -- this invention electrode and the reference electrode were produced like the example 1 except having used the active material (each cobalt hydroxide being 10 weight sections) of the calcium hydroxide in the conductive layer to the nickel hydroxide 100 weight section which is 0 weight section, the 0.3 weight sections, the 0.5 weight sections, the 1.5 weight sections, 2 weight sections, the 2.5 weight sections, or 3 weight sections comparatively.

Subsequently, the trial cel was assembled like the point using these this invention electrode and the reference electrode. And charge and discharge were carried out on the same conditions as the point, the utilization factor of an active material was searched for from said formula, and the relation of the rate of a calcium hydroxide and the utilization factor of an active material over nickel hydroxide was investigated. A result is shown in drawing 2 . In addition, the result about this invention electrode NA1 (calcium-hydroxide 1 weight section) is also shown in drawing 2 .

[0032] drawing 2 -- the utilization factor of the active material of each electrode, and the cobalt hydroxide in a conductive layer -- comparatively -- \*\* -- relation -- an axis of ordinate -- the utilization factor (%) of an active material -- moreover, it is the graph by which weight number of copies of the calcium hydroxide in the conductive layer to the nickel hydroxide 100 weight section was taken and shown on the axis of abscissa, and as shown in this drawing, when the rate of a calcium hydroxide to the nickel hydroxide 100 weight section is made into 0.5 - 2 weight section, it turns out that the utilization factor of an active material can be made high.

[0033]

[Effect of the Invention] The pack density and the utilization factor of an active material are high. So, high capacity-ization of cell capacity is attained by using as a nickel positive electrode of an alkaline battery.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the graph of the cobalt hydroxide in the conductive layer to the nickel hydroxide 100 weight section which shows relation with the utilization factor (%) of an active material comparatively (weight section).

[Drawing 2] It is the graph of the calcium hydroxide in the conductive layer to the nickel hydroxide 100 weight section which shows relation with the utilization factor (%) of an active material comparatively (weight section).

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[Translation done.]



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-201327

(43) 公開日 平成7年(1995)8月4日

(51) Int.Cl.<sup>8</sup>

識別記号

庁内整理番号

F I

技術表示箇所

H 0 1 M 4/32

審査請求 未請求 請求項の数 1 F D (全 5 頁)

(21) 出願番号 特願平5-352525

(22) 出願日 平成5年(1993)12月29日

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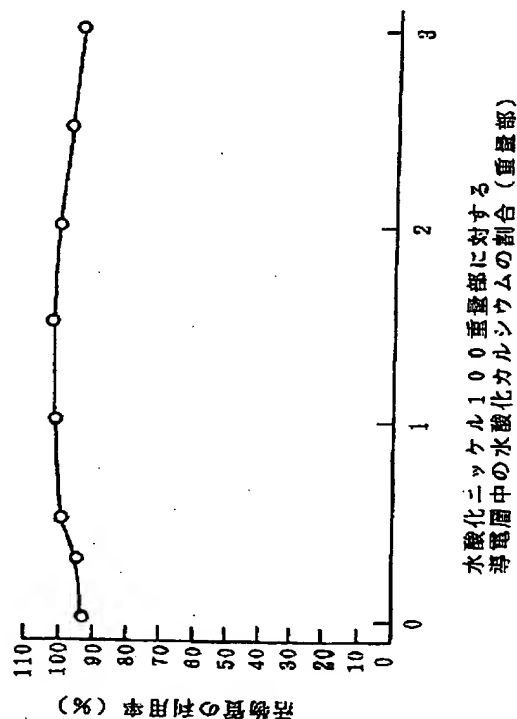
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(54) 【発明の名称】 アルカリ蓄電池用の非焼結式ニッケル正極

(57) 【要約】

【構成】3次元多孔質構造を有する集電体の孔内に活物質を充填してなるアルカリ蓄電池用の非焼結式ニッケル正極において、前記活物質として、平均粒径7~12 $\mu$ mの水酸化ニッケル100重量部の粒子表面に、水酸化カルシウム0.5~2重量部と水酸化コバルト5~15重量部とからなる導電層が形成されたものが用いられている。

【効果】活物質の充填密度及び利用率が高い。それゆえ、アルカリ蓄電池のニッケル正極として用いることにより、電池容量の高容量化が可能となる。



## 【特許請求の範囲】

【請求項1】3次元多孔質構造を有する集電体の孔内に活物質を充填してなるアルカリ蓄電池用の非焼結式ニッケル正極において、前記活物質が、平均粒径 $7\sim 12\mu\text{m}$ の水酸化ニッケル100重量部の粒子表面に、水酸化カルシウム0.5～2重量部と水酸化コバルト5～15重量部とからなる導電層が形成されたものであることを特徴とするアルカリ蓄電池用の非焼結式ニッケル正極。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明はアルカリ蓄電池用の非焼結式ニッケル正極に係わり、詳しくは活物質の充填密度及び利用率が高いアルカリ蓄電池用の非焼結式ニッケル正極を得ることを目的とした、前記活物質の改良に関する。

## 【0002】

【従来の技術及び発明が解決しようとする課題】水酸化ニッケルを活物質とする非焼結式ニッケル正極がニッケル-カドミウム蓄電池等のアルカリ蓄電池の正極として実用化されている。上記水酸化ニッケルの製造方法としては、硝酸ニッケルをアルカリ水溶液中に投入し、攪拌混合しつつ反応させて、球状の水酸化ニッケルを沈殿物として得る方法が提案されている。しかしながら、この方法により得た水酸化ニッケルを、そのまま活物質として用いた正極には、水酸化ニッケルの導電性が良くないために正極の利用率が低く、それゆえ容量が小さいという問題があった。

【0003】この問題を解決するべく、アルカリ水溶液中に硝酸ニッケル水溶液とともに硝酸カルシウムを投入し、水酸化ニッケルと水酸化カルシウムとを共沈させて、水酸化ニッケルの粉末中に導電性を向上させるべく水酸化カルシウムを含有せしめる方法が提案されている（共沈法）。

【0004】しかしながら、この共沈法により作製した水酸化カルシウム含有水酸化ニッケルは、上述した水酸化ニッケルを単独で沈殿させる方法により作製した水酸化ニッケル（通常、粒径 $6\mu\text{m}$ 程度以上）に比べて粒径が $2\sim 3\mu\text{m}$ と小さく、また嵩密度も小さいため、これを活物質として用いた非焼結式ニッケル正極には、活物質の充填密度が低いという問題があった。

【0005】また、共沈法により作製した場合、水酸化カルシウムが活物質（水酸化カルシウム含有水酸化ニッケル）の表面のみならず内部にも分散して存在するため、導電性はさほど向上せず、それゆえ活物質の利用率もまたさほど向上しないという問題があった。この問題については、活物質（水酸化カルシウム含有水酸化ニッケル）を含むスラリー中に水酸化コバルト等の導電剤を別途添加混合して、スポンジ状又は繊維状の3次元多孔質構造を有する集電体の孔内に充填する試みが提案されているが、水酸化コバルトと水酸化カルシウム含有水酸

化ニッケルとを集電体の孔内に均一に分散させることは至難であるため、活物質の利用率が十分に高いニッケル正極を得るには到っていないのが実情である。

【0006】本発明は、以上の事情に鑑みなされたものであって、その目的とするところは、活物質の充填密度及び利用率が高いアルカリ蓄電池用の非焼結式ニッケル正極を提供するにある。

## 【0007】

【課題を解決するための手段】上記目的を達成するための本発明に係るアルカリ蓄電池用の非焼結式ニッケル正極（以下、「本発明電極」と称する。）は、3次元多孔質構造を有する集電体の孔内に活物質を充填してなるアルカリ蓄電池用の非焼結式ニッケル正極において、前記活物質が、平均粒径 $7\sim 12\mu\text{m}$ の水酸化ニッケル100重量部の粒子表面に、水酸化カルシウム0.5～2重量部と水酸化コバルト5～15重量部とからなる導電層が形成されたものである。

【0008】水酸化ニッケルの平均粒径は $7\sim 12\mu\text{m}$ に規制される。これは、 $7\mu\text{m}$ 未満の場合は、活物質の粒径が小さ過ぎて集電体の孔内に充填し難くなるとともに、嵩密度が小さくなるため、一方 $12\mu\text{m}$ （導電層の膜厚は通常 $1\mu\text{m}$ 程度であるので、この場合の活物質粒子の平均粒径は通常 $13\mu\text{m}$ 程度となる。）を越えた場合は、水酸化ニッケルの嵩密度は大きくなるものの、粒径が大き過ぎて集電体の孔内に充填し難くなるため、いずれの場合も活物質の充填密度が低くなるからである。

【0009】水酸化ニッケルは、硝酸ニッケル、硫酸ニッケルなどをアルカリ水溶液中に投入し攪拌混合することにより沈殿物として得られる。平均粒径 $7\sim 12\mu\text{m}$ の水酸化ニッケルを得るには、アルカリ水溶液のpH、攪拌速度、攪拌時間などを適宜調整する必要がある。例えば、平均粒径が $7\mu\text{m}$ の水酸化ニッケル粉末を作製する場合には、アルカリ水溶液のpHを $11\pm 0.1$ 、攪拌速度を $400\text{rpm}$ 、攪拌時間を12時間とすればよく、平均粒径が $12\mu\text{m}$ の水酸化ニッケル粉末を作製する場合には、アルカリ水溶液のpH $11\pm 0.1$ 、攪拌速度 $800\text{rpm}$ 、攪拌時間60時間とすればよい。

【0010】導電層中の水酸化カルシウムの割合が水酸化ニッケル100重量部に対して0.5～2重量部に規制されるのは、0.5重量部未満の場合は、導電性が未だ充分でないため、活物質の利用率が十分に向上せず、一方2重量部を越えた場合は、活物質中の水酸化ニッケルの割合が少なくなり、容量の低下を招くからである。

【0011】また、導電層中の水酸化コバルトの割合が水酸化ニッケル100重量部に対して5～15重量部に規制されるのも、上記と同じ理由による。すなわち、5重量部未満の場合は、導電性を十分に高めることができないため、活物質の利用率の向上が十分に達成されず、一方15重量部を越えた場合は、活物質中の水酸化ニッケルの割合が少なくなり、容量の低下を招くからであ

る。

【0012】

【作用】適度の粒径の活物質が用いられているので、活物質の充填密度が高くなる。また、活物質の表面に、所定量の水酸化カルシウムと水酸化コバルトとを含有する導電層が存在するので、活物質の導電性が向上し、その結果ニッケル正極の活物質の利用率が高くなる。

【0013】

【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例により何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

【0014】（実施例1）硝酸ニッケル水溶液を、水酸化ナトリウム及びアンモニアにてpH11±0.1に調整した水溶液中に投入して、600rpmで攪拌混合しつつ24時間反応させて、球状の水酸化ニッケルを得た。

【0015】次いで、上記水酸化ニッケル粉末と硝酸コバルト水溶液と硝酸カルシウム水溶液とを、水酸化ナトリウム及びアンモニアにてpH11±0.1に調整した水溶液中に投入して、600rpmで攪拌混合しつつ24時間反応させて、水酸化ニッケルの粒子表面に、水酸化コバルトと水酸化カルシウムとからなる導電層を形成し、これを水洗、乾燥して、活物質を得た。

【0016】導電層中の水酸化ニッケル100重量部に対する水酸化コバルト及び水酸化カルシウムの割合を1CPにより分析したところ、それぞれ10重量部及び1重量部であった。なお、後述する各金属の比率も全て1CPにより分析したものである。

【0017】次に、上記活物質100重量部と、増粘剤（電極作製後は結着剤として働く。）としてのカルボキシメチルセルロース0.5重量部の水溶液とを混練してスラリーとし、このスラリーを発泡メタルに充填して、本発明電極NA1を作製した。

【0018】（比較例1）硝酸ニッケル水溶液と硝酸コバルト水溶液と硝酸カルシウム水溶液とを、ニッケル：コバルト：カルシウムのモル比98：1：1で、水酸化ナトリウム及びアンモニアにてpH11±0.1に調整した水溶液中に投入して、600rpmで攪拌混合しつつ24時間反応させて、水酸化ニッケルと水酸化コバルトと水酸化カルシウムとを共沈させ、この共沈物を水洗、乾燥して、活物質を得たこと以外は上記実施例1と同様にして、比較電極NB1を作製した。

【0019】〔活物質の利用率〕本発明電極NA1及び比較電極NB1を用いて、後述の如く試験セルを組み立て、この試験セルを1/10Cの電流で16時間充電し

た後、1/3Cの電流で放電終止電圧0.8Vまで放電して、各試験セルの放電容量を測定し、下記算出式に基づいて、各試験セルの正極の活物質の利用率を求めた。結果を、表1に示す。

【0020】＜試験セルの組立＞本発明電極NA1及び比較電極NB1を試験電極（正極）とし、この試験電極に対して充分大きな電気化学容量を持つペースト式カドミウム極を対極としてナイロンセパレータを介して完全対向する形で重ね合わせる。これをポリエチレン袋に入れ両側より構成圧（40Kgf）をかける。これに比重1.23KOH水溶液を入れ開放型単極セルを作製した。

【0021】＜活物質の利用率の算出式＞

活物質の利用率（％）＝試験セルの放電容量（mAh）×100／〔活物質重量（g）×単位活物質重量あたりの理論容量（mAh/g）〕

単位活物質重量あたりの理論容量（mAh/g）＝構成物質1（Ni（OH）<sub>2</sub>）の理論容量×活物質1gあたりの構成物質1の重量（wt％）＋構成物質2（Co（OH）<sub>2</sub>）の理論容量×活物質1gあたりの構成物質2の重量（wt％）＋構成物質3（Ca（OH）<sub>2</sub>）の理論容量×活物質1gあたりの構成物質3の重量（wt％）

【0022】例えばNi（OH）<sub>2</sub>289.0mAh/g、Co（OH）<sub>2</sub>288.3mAh/g、Ca（OH）<sub>2</sub>2723.4mAh/gである。

【0023】

【表1】

電極	活物質の利用率（％）
NA1	102
NB1	95

【0024】表1に示すように、本発明電極NA1は活物質の利用率が102％と高いのに対して、比較電極NB1は活物質の利用率が95％と低い。

【0025】〔活物質の平均粒径、活物質のタップ嵩密度及び活物質の充填密度〕本発明電極NA1及び比較電極NB1の各正極の作製に用いた活物質のフィシャーサイズでの平均粒径及びタップ嵩密度と、本発明電極NA1及び比較電極NB1の活物質の充填密度とを調べた。結果を表2に示す。なお、本発明電極NA1に用いた活物質では導電層を形成する前の水酸化ニッケル自体の平均粒径及びタップ嵩密度も調べたので、その結果も表2に併せて示す。

【0026】

【表2】

電極		平均粒径 ( $\mu\text{m}$ )	タップ嵩密度 ( $\text{g/cc}$ )	充填密度 ( $\text{g/cc}$ )
NA1	水酸化ニッケル	9.1	2.3	—
	活物質	9.5 ~ 10.1	2.4 ~ 2.6	2.80
NB1		3.2	1.3	2.10

【0027】本発明電極NA1の活物質の充填密度は $2.80\text{g/cc}$ と高いのに対して、比較電極NB1の活物質の充填密度は $2.10\text{g/cc}$ と低い。これは、次に示す理由による。

【0028】本発明電極NA1に用いた水酸化ニッケルの平均粒径は $9.1\mu\text{m}$ であり、また活物質の平均粒径は $9.5 \sim 10.1\mu\text{m}$ である。いずれも平均粒径が大きい。また、水酸化ニッケルのタップ嵩密度は $2.3\text{g/cc}$ であり、また活物質のタップ嵩密度は $2.4 \sim 2.6\text{g/cc}$ である。いずれもタップ嵩密度が大きい。これに対して、比較電極NB1に用いた活物質の平均粒径は $3.2\mu\text{m}$ と小さく、またタップ嵩密度が $1.3\text{g/cc}$ と小さい。本発明電極NA1と比較電極NB1の活物質の充填密度の差は、このような平均粒径及び嵩密度の大小によるものである。

【0029】〔水酸化ニッケルに対する水酸化コバルトの割合と活物質の利用率との関係〕水酸化ニッケル100重量部に対する水酸化コバルトの割合が、0重量部、5重量部、15重量部又は20重量部である活物質（水酸化カルシウムはいずれも1重量部）を用いたこと以外は実施例1と同様にして、本発明電極及び比較電極を作製した。次いで、これら本発明電極及び比較電極とを用いて、先と同様にして試験セルを組み立てた。そして、先と同じ条件で充放電して活物質の利用率を上述の算出式から求め、水酸化ニッケルに対する水酸化コバルトの割合と活物質の利用率との関係を調べた。結果を図1に示す。なお、図1には、本発明電極NA1（水酸化コバルト10重量部）についての結果も示してある。

【0030】図1は各電極の活物質の利用率と導電層中の水酸化コバルトの割合との関係を、縦軸に活物質の利用率（％）を、また横軸に水酸化ニッケル100重量部に対する導電層中の水酸化コバルトの重量部数をとって示したグラフであり、同図に示すように水酸化ニッケル100重量部に対する導電層中の水酸化コバルトの割合を5～15重量部とした場合に活物質の利用率を高くす

ることができることが分かる。

【0031】〔水酸化ニッケルに対する水酸化カルシウムの割合と活物質の利用率との関係〕水酸化ニッケル100重量部に対する導電層中の水酸化カルシウムの割合が、0重量部、0.3重量部、0.5重量部、1.5重量部、2重量部、2.5重量部又は3重量部である活物質（水酸化コバルトはいずれも10重量部）を用いたこと以外は実施例1と同様にして、本発明電極及び比較電極を作製した。次いで、これら本発明電極及び比較電極を用い、先と同様にして試験セルを組み立てた。そして、先と同じ条件で充放電して活物質の利用率を前記算出式から求め、水酸化ニッケルに対する水酸化カルシウムの割合と活物質の利用率との関係を調べた。結果を図2に示す。なお、図2には、本発明電極NA1（水酸化カルシウム1重量部）についての結果も示してある。

【0032】図2は各電極の活物質の利用率と導電層中の水酸化コバルトの割合との関係を、縦軸に活物質の利用率（％）を、また横軸に水酸化ニッケル100重量部に対する導電層中の水酸化カルシウムの重量部数をとって示したグラフであり、同図に示すように水酸化ニッケル100重量部に対する水酸化カルシウムの割合を0.5～2重量部とした場合に活物質の利用率を高くすることができることが分かる。

【0033】

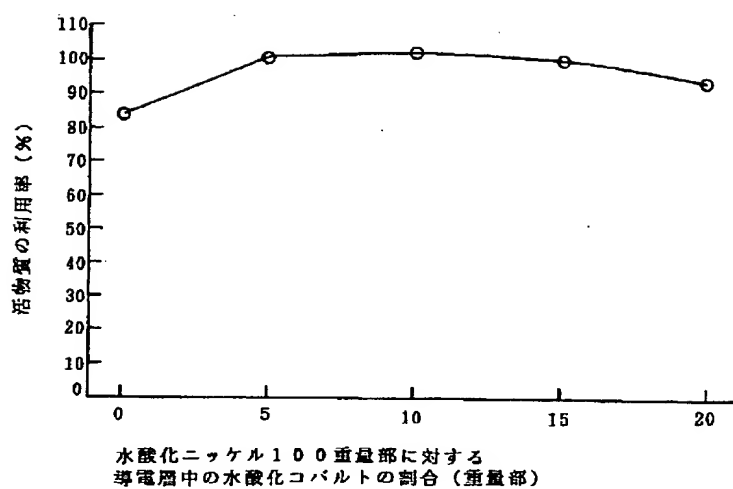
【発明の効果】活物質の充填密度及び利用率が高い。それゆえ、アルカリ蓄電池のニッケル正極として用いることにより、電池容量の高容量化が可能となる。

【図面の簡単な説明】

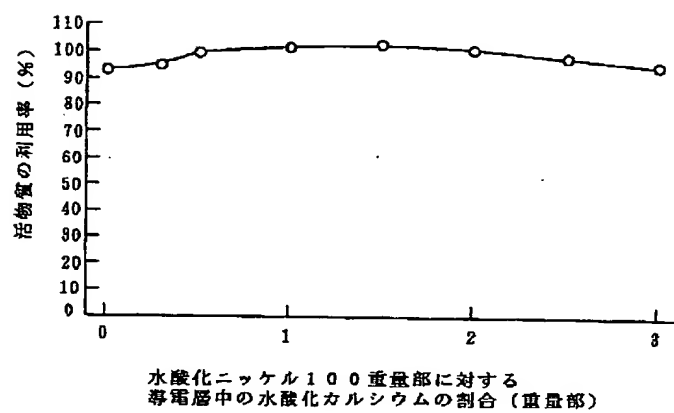
【図1】水酸化ニッケル100重量部に対する導電層中の水酸化コバルトの割合（重量部）と活物質の利用率（％）との関係を示すグラフである。

【図2】水酸化ニッケル100重量部に対する導電層中の水酸化カルシウムの割合（重量部）と活物質の利用率（％）との関係を示すグラフである。

【図1】



【図2】



フロントページの続き

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